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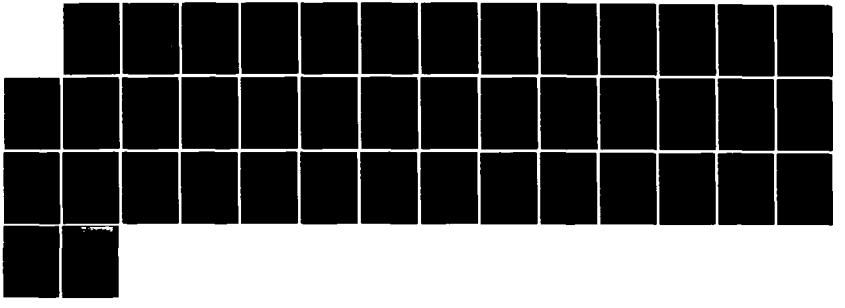

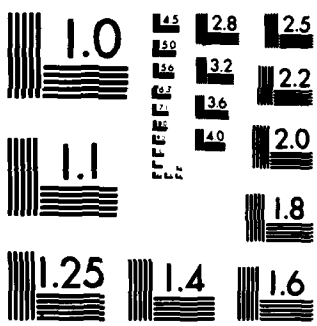

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An extensive study was conducted on the swaging of composite wires consisting of an intercalated graphite core in a copper sheath. The purpose was to develop a method that replicated earlier results wherein high electrical conductivity was encountered. The project was unable to produce those earlier, favorable results. It was determined that analysis of core resistivity cannot be done where the core has a higher resistivity than the sheath. Copper chloride was shown to be an air stable intercalant in graphite with a

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University of Pennsylvania
The Moore School of Electrical Engineering
Philadelphia, PA 19104

Final Report on

Development of Intercalated Wire and Cable

Contract No. DAAK 70-79-C-0244

to

Mobility Equipment Research and Development Command
Ft. Belvoir, Virginia 20060

Principal Investigator: F. Lincoln Vogel

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Abstract

An extensive study was conducted on the swaging of composite wires consisting of an intercalated graphite core in a copper sheath. The purpose was to develop a method that replicated earlier results wherein high electrical conductivity was encountered. The project was unable to produce those earlier, favorable results. It was determined that analysis of core resistivity cannot be done where the core has a higher resistivity than the sheath. Copper chloride was shown to be an air stable intercalant in graphite with a crystal resistivity in the vicinity of 5×10^{-6} ohm cm. The main problem of swaging cored tube samples remains unsolved.

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I. General Introduction

It has been known for many years that the electrical conductivity of graphite is enhanced by intercalation with the electron donors of Group I of the Periodic Table (1), and with the advent of intercalation with the strong mineral acid acceptors such as nitric acid (2), the possiblity of creating practical conductors came into view. This possibility appeared more promising after a series of experiments which appeared to demonstrate electrical conductivities comparable to those of the best metals, silver and copper, and in a filamentary form suitable for engineering applications. The first experiments which showed the extraordinarily high conductivity in relatively perfect artificial graphite crystals, referred to as highly oriented pyrolytic graphite (HOPG), employed arsenic pentafluoride as the intercalant (3,4). The experiments which put the conducting material into a filamentary form, useful for engineering applications, employed antimony pentafluoride as the graphite intercalant (4,5,6). Both of these intercalants had as attributes that of being strong Lewis acids. The low density of these compounds compared to copper, i.e. < 3.0 g/cm^3 vs. 8.9 g/cm^3, offered an additional advantage for most engineering applications but particularly those in the military.

As promising as these discoveries were, problems soon appeared. Investigators were unable to reproduce the high electrical conductivities of the AsF_5 intercalated HOPG- even investigators in the laboratory at Penn, where the first experiments were executed, and while the original wire experiment has been replicated twice (6), no one recently has been able to successfully swage an intercalated graphite-filled copper ampoule to final wire size because of longitudinal splitting. Attempts have been made to

substitute wire drawing for the swaging (7) but these have been unsuccessful. It appears that the radial pressure of the swaging may be an essential ingredient to the process and that the longitudinal tension of wire drawing causes transverse cracking in the brittle graphite phase of the composite wire.

While the questions of the reproducibility of the high conductivity intercalation of graphite are being examined in a companion program, Contract No. DAAK-70-82-C-0049, this work concentrated on the fabrication of an intercalated graphite-copper sheathed wire by swaging. This approach was taken in this project for two reasons: 1) only swaging had been observed to produce a satisfactory result and 2) this result was in a useful form- a wire conductor.

The main problems to be dealt with here are the continuity of the compacted powder core of the intercalated graphite composite wire, and splitting of the wire during swaging. Essential background information is to be found in reference 6.

II. Investigation of Fundamentals in Composite Wire Fabrication

A. Synthesis of Intercalated Graphite

1. Introduction

Obviously, the most important factor in the conductivity of a metallic solid is the electrical conductivity of the crystal itself. This depends on the fundamental quantities n, the charge carrier density and μ, the carrier mobility according to

$$\sigma = ne\mu$$

where σ = electrical conductivity and e is the electronic charge. The mobility would have a maximum value in a perfect crystal at absolute zero so at normal temperatures and with less than perfect crystals additional scattering results. This section attempts to evaluate some of these factors for the case of intercalated graphite powder in a composite wire.

Large crystals of nitric acid intercalated graphite are probably the most studied electrically conducting graphite composition (2,8) and while many chemical studies have been made on powders very few measurements of the polycrystalline electrical resistivities have been made. These are attempted here.

Atmospheric stability is also an important characteristic for practical conductors of electricity and this characteristic is notoriously absent for most of the intercalated graphite compounds that have been studied to date. Thus, the revelation (9) that $CuCl_2$ intercalated graphite is entirely stable in air and water at room temperature and abcve immediately stimulated our interest to examine its electrical resistivity. A difficulty that was encountered in this regard was that while graphite powders were made to intercalate, larger crystals such as HOPG could not be successfully treated.

2. Nitric Acid Intercalation

The first nitric acid intercalation experiment was done on Superior #1601 flake graphite with liquid acid. The reasons for a liquid phase treatment were that this method has been used successfully with graphite fibers (10,11) and also that no special glassware would be required.

Three ml. of freshly-prepared nitric acid were distilled into a twelve ml. graduated cold finger. These three ml. were then distilled into a tube containing 1.26 grams of Superior #1601 graphite and left for one hour at room temperature. The 1601 graphite had previously been heated at 150°C. in a vacuum to drive off any water, which would react with the nitric acid. The liquid was then distilled back into the cold finger. Unfortunately, most of the nitric acid stayed with the graphite, and had to be pumped off with a vacuum pump. This made it impossible to determine the amount of nitric acid which had intercalated into the graphite. The intercalated graphite powder was then pressed, in a dry box, for resistivity measurements. However, it tended to flow out of the press in ribbons, so standard samples could not be made. The powder was then pumped on over a period of two days to remove some of the intercalated nitric acid, and was successfully pressed into samples. The results follow in Table I.

Table I. Electrical Resistivity of Pressed Graphite Powder Intercalated With Liquid Nitric Acid

Material	Pressure(pounds)	ρ (micro ohm-cm)	Density(gm/cc)
HNO_3 → 1601	2000	308	1.82
	3000	245	2.04
1601	4000	380	2.18
	5000	348	2.18

A vapor phase nitric acid intercalation of Superior #2135 graphite was performed. Freshly prepared nitric acid was distilled into a pyrex tube containing a ground glass frit upon which the graphite had been placed. The nitric acid liquid was allowed to stand overnight at $0^{o}C$ while its vapor intercalated the graphite. The acid was then removed with a vacuum pump.

A pressing of this material was attempted in order to determine its resistivity relative to other intercalated compounds. This could not be done, however, because the powder tended to flow out of the die under pressure.

This extraordinary property is indicative of the very good plastic flow of intercalated graphite. The intercalated layer reduces the shear stress necessary for deformation along the basal planes and in effect lubricates their motion. As a result a die and plunger of extremely close tolerances are needed to obtain a satisfactory pressing.

The intercalated graphite was also extruded into a copper tube, inside a dry box, and the tube was swaged. Although the tube cracked relatively early the following results were obtained after swaging:

Table II Electrical Resistivity of Swaged Graphite Powder Intercalated With Nitric Acid

ρ(composite)	ρ(core)	Core Density
2.25 μΩ	98.4 μΩ	3.97 g/cc

3. Copper Chloride Intercalation

Through a visit to Dr. Eberhard Stumpp's laboratory in Clausthal, West Germany, information was obtained on the synthesis of copper chloride intercalation of graphite powder. Stumpp used a natural graphite, mined

in Germany and similar to Superior 2135. The graphite powder is mixed with copper chloride hexahydrate and heated gently in a flask to 400°C under a stream of chlorine. This continues for several days and then the result is washed in hot running water to remove the excess copper chloride. X-Ray diffraction indicates stage one compound for the time and temperature conditions described above. The pressed pill resistivity was 200 μΩ cm at a density of 2.8 g/cm^3.

The following procedure was developed in our lab for the closed tube synthesis of the stage two compound.

First, Superior 1601 graphite powder is mixed in air with enough $CuCl_2 \cdot 6H_2O$ to produce a stage 1 compound. The mixture is heated in a vacuum to drive off any H_2O, and is then sealed at room temperature in a pyrex tube with Cl_2 gas to provide a proper reducing atmosphere. The pyrex tube is then heated at 350° - 400°C for 24 hours. The tube is cooled, opened under a hood, and the powder is washed with deionized H_2O to remove any unintercalated $CuCl_2$. To drive off this wash water the powder is heated overnight in a vacuum.

Still another variation was practiced in our labs to avoid the inconvenience of sealed tubes, to shorten the heating time and to permit larger sample sizes. A horizontal tube furnace capable of 500°C was fitted with a gas system capable of handling chlorine and nitrogen. The mixed powders (3 grams of $CuCl_2 \cdot 6H_2O$ per two grams of graphite) are loaded into an open boat in the tube of the furnace. The air is flushed out with nitrogen flow and the temperature raised to 100 - 150°C to dehydrate the copper chloride. The gas flow is switched to chlorine and the temperature raised to 480 - 500°C. Since the pyrex glassware used would soften at 560°C, care must be taken to avoid overheating. With quartz ware the

the temperature could be raised to 900°C with the benefit of much shorter treatment times. At 480°, treatment times of less than 24 hours were experienced. To cool, the gas is swtiched from Cl_2 to N_2 and the power shut off. After the powder reaches room temperature, it is removed from the furnace and washed as before.

The best evaluation of the in plane electrical resistivity of intercalated graphite composition is done on highly oriented pyrolytic graphite (HOPG) or large single crystal flakes. There are no accounts of such experiments in the published literature and so an attempt was made at such a determination in collaboration with Professor Stumpp. Samples of HOPG were cut and cleaved to 0.5 cm x 0.5 cm x 0.25 mm thick and resistivity measured using the rf induction method. These were sent to Prof. Stumpp for intercalation in the usual way. After many months of trials the information was returned to us that no significant intercalation could be made to occur as judged by weight or thickness change or x-ray diffraction. This negative information prompted several trials on our part using the sealed tube method described previously. The results of the first experiment are summarized in the following table:

Table III Intercalation of HOPG With $CuCl_2$ at 350 - 400°C

Date	Mass(mg)	Edge Thickness(mm)	Resistivity ρ (micro ohm cm)
2/12/80 (original sample)	8.0	.145	38.9
2/25/80 (1st intercalation)	9.0	.254	26.3
5/8/80 (2nd intercalation)	9.8	.245	22.2

It is evident from these data that intercalation is proceeding, albeit very slowly. However, the mass showed an increase, the sample thickness increased although only at the edges and the in-plane rf

resistivity (11) showed a decrease, although the measured value is distorted by the fact that the sample is not of uniform thickness. It appears that while the chemical reaction is initiated at the edge planes of the sample it is retarded by induced stresses. For a small particle these stresses are small but for a large sample they are significant. After these experiments were finished, Woollam (12) discovered that raising the temperature to 800 - 900^{o}C allows the intercalation to proceed in large samples.

A second experiment was executed wherein HOPG was treated with $CuCl_2$ in a chlorine atmosphere in an ampoule at 470^{o}C. Results are shown in Table IV.

Table IV Intercalation of HOPG With $CuCl_2$ at 470^{o}C

Date	Mass(mg)	Edge Thickness(mm)	Resistivity ρ (micro ohm cm)
2/12/80 (Original Sample #1)	8.0	0.145	38.9
2/25/80 (1st intercalation)	9.0	0.254	26.3
5/8/80 (2nd intercalation)	9.8	0.245	22.2
10/1/80 (3rd intercalation)	15.61	0.385	34.8
9/6/80 (Original Sample #2)	10.0	0.195	43.9
10/1/80 (1st intercalation)	22.8	0.531	38.4

Again it is evident that intercalation is limited to the edge regions of the samples. The same precautions must be exercised in the interpretation of these data as were suggested before.

4. Conclusions

The appearance of $CuCl_2$ intercalated graphite having a high degree of atmospheric stability is an important revelation. More will be said in a later section concerning its electrical conductivity with implications for use as a practical conductor.

II.B. Pressed Powder Experiments

1. Introduction

While the electrical conductivity of the crystal is probably the most important factor in the suitability for any material as a practical conductor of electricity, the way that the crystals come into contact is also of great importance. The boundary effects that occur are graphically illustrated in a previous report, Reference 6, Part II, Figure 7 on page II-17. It is seen here that pure copper powder with a crystal resistivity of 1.7×10^{-6} ohm cm has in the pressed powder form a resistivity which is in the range of 50 to serveral hundred micro ohm cm and is a function of the pressed density. Apparently, in the as-pressed condition there are numerous physical and chemical factors acting at the crystal boundaries to increase the resistivity markedly. However, after annealing in hydrogen the resistivity drops markedly and while still a function of density, the annealed resistivity extrapolates to 1.7×10^{-6} ohm cm at the ideal density of 8.95 g/cm^3. The hydrogen anneal removes the chemical and physical factors responsible for the boundary scattering of charge carriers. Similar behavior can be expected for the core of a composite wire consisting of intercalated graphite powder sheathed in copper.

The following experiments were designed to gain a direct measurement of the electrical resistivity of intercalated graphite powder when compacted into a solid body. This matter has been treated in other parts of this program and the methods used have already been reported. Therefore the reader is referred to Reference 6 for some important basic considerations and to Reference 11 for the techniques used for forming and measuring pressed intercalated graphite.

2. Graphite

As a basis for comparison, pristine graphite powder, Superior No. 2135, a natural flake graphite known to react well to intercalation, was pressed into 5 mm diameter cylinders at a series of pressures and subsequently measured by the rf method for electrical resistivity. Table V lists the results.

Table V Electrical Resistivity of Superior 2135 Pressed Powder

Pressure Pounds/in^2	Density grams/cm^3	Electrical Resistivity micro ohm cm
66,000	2.01	1903
99,000	1.97	1725
131,000	--	1910

It is perhaps surprising that in this case of pristine graphite higher pressure did not produce higher density and consequently lower electrical resistivity. However, referring to Reference 6 II, Figure 7 we see that these data compare favorably with the copper case. For copper powder pressed to 70% of its ideal density the resistivity is ~ 100 times the ideal resistivity where for the case of the 2135 graphite the factor is ~ 50 times.

We were notified by Superior graphite that the natural graphite, #2135 would not be available in the future which led to an examination of a suitable substitute. The following table shows similar data as before on Lonza KS 44, a high quality synthetic flake graphite.

Table VI Electrical Resistivity of Lonza KS 44 Pressed Powder

Pressure Pounds/cm^2	Density grams/cm^3	Electrical Resistivity micro ohm cm
66,000	1.86	1672
99,000	1.91	1619

This shows that the Lonza KS 44 has a somewhat more regular density behavior and slightly lower resistivity, consistent with its claimed high quality.

3. Copper Chloride Intercalated Graphite Powder

Superior #2135 and Lonza KS 44 powders were intercalated to stage II with copper chloride using the closed tube method described in II A 3 of this report as a way of estimating the crystal resistivity of the graphite intercalation compound. Results are summarized in Table VII.

Table VII Electrical Resistivity of Copper Chloride Intercalated Graphite Powders

Graphite	Pressure $_3$ Pounds/cm^3	Density $_3$ grams/cm^3	Electrical Resistivity micro ohm cm
2135	66,000	2.27	766
2135	99,000	2.23	688
2135	132,000	--	661
2135	165,000	--	655
KS44	66,000	2.43	522
KS44	99,000	2.38	511

These data lead us to estimate that $CuCl_2$ intercalated graphite has an in-plane electrical resistivity roughly comparable to ferric chloride intercalated graphite, i.e. 5 micro ohm cm at stage two. Attempts were made to vacuum anneal at 500^{0}C the intercalated compacts to improve crystal to crystal contact. Uniformly the resistivity increased indicating degradation of the intercrystalline areas.

4. Super Acid Intercalation of Graphite

One set of experiments was done intercalating Superior #2135 graphite

powder to stage two with the super acid HF + SbF_5 using the ampoule methods described in Reference 11 Section II-B. The powders, being air sensitive were pressed using the methods described in Section IV B 5 of the foregoing reference. Results are shown in Table VIII.

Table VIII Electrical Resistivity of Superior 2135 Graphite Powder Intercalated With HF · SbF_5

Pressure Pounds/In^2	Density Grams/cm^3	Electrical Resistivity micro ohm cm
66,000	2.41	871
99,000	2.37	806

These data are consistent with the generally accepted opinion now that almost all strong acids, Bronsted or Lewis, when intercalated into graphite result in an in-plane resistivity of 4-6 micro ohm cm at stage two (13).

5. Anisotropy Measurements

Measurements of electrical resistivity were made on KS 44 and 2135 powders, both pristine and intercalated with $CuCl_2$, pressed into cubes ½ cm on a side. Resistivities were taken both parallel and normal to the pressing direction with parallel designated as $\vec{c}$ axis resistivity because that is the alignment of the crystallographic planes caused by uniaxial compression. It is realized however that the alignment of the planes is not perfect but somewhere between 60% and 80% (see ref. 6). Data are tabulated as follows:

Table IX $\vec{c}$ and $\vec{a}$ axis Electrical Resistivities of Pristine and $CuCl_2$ Intercalated and Pressed Graphite Powders

Graphite Powder	Intercalant	Pressure Pounds/in^2	Electrical Resistivity micro ohm cm	Ratio $\rho c/\rho a$
KS 44	None	66,000	5580	3.34
KS 44	None	99,000	5380	3.32
2135	None	66,000	9330	4.90
2135	None	99,000	9860	5.70
KS44	$CuCl_2$	66,000	1610	3.08
KS44	$CuCl_2$	99,000	2140	4.12
2135	$CuCl_2$	66,000	3860	5.22
2135	$CuCl_2$	99,000	5820	8.53

From these data it appears that the anisotropy ratio of the graphite compacts is increased by pressure and intercalation.

6. Conclusions

The powder experiments indicate intercalated crystal in-plane resistivities of 4-6 micro ohm cm but attempts to achieve these values in annealed compacts in the manner of pressed copper have not been successful. Pressed compacts do however show a measure of crystal anisotropy.

III. Fabrication of Composite Wires

A. Extrusion Filling of Ampoules

1. Introduction

While obviously the most important problem in the fabrication of the composite wires is the longitudinal splitting that occurs during swaging, filling of the ampoule at the start carries with it certain difficulties. Graphite powder, being light, fluffy and lubricating, is difficult to pack to a density approaching 50% of the ideal. Also any tamping of the graphite in the ampoule to increase the packing density would have the effect orienting the basal planes of the graphite normal to the longitudinal axis so that: 1) shear deformation cannot occur easily and 2) a full 90% rotation of the basal planes must take place during swaging. On the other hand, if filling were made to take place by extrusion- as in squeezing toothpaste from a tube, then both the orientation and densification could be made to take place most conveniently. The following experiments were executed to examine that possibility.

2. Die Design

The first die was a simple cylindrical steel construction having a cavity 3/4" in diameter x 3" long having a tightly fitting steel plunger. The cavity had a 30^{0} taper down to the die opening which was 0.160" in diameter, intended to extrude a diameter rod which would fit snugly into the copper ampoule (See Figure 13 of reference 11). In operation the extrusion die and ampoule were aligned and clamped in position with the open end of the ampoule at the die opening.

Problems arose sometimes with alignment and contact between die and ampoule so that the extrudate would leak out of the intervening space.

This was remedied by machining an indentation for the ampoule at the die opening such that when the open end of the ampoule was inserted the ampoule cavity was aligned to receive the extrudate and the two parts were close enough not to allow material to escape.

At a later stage of the program in an effort to avoid the longitudinal splitting of the wires that was occurring during swaging, the inside diameter of the ampoules was increased to 0.180 inches, while keeping the outside diameter the same (0.250 inches). This modification necessitated a third change in the extrusion die, i.e. expanding the opening to 0.175 inches.

3. Pressure Effects

The effect of extrusion pressure on the final result (swaged wire) was examined in two experiments, one on pristine graphite and one on intercalated graphite. Results are given in the two following tables.

Table X Resistivity of Swaged Wires Filled With Superior 2135 Graphite

Filling Pressure Pounds/in^2	Core Density % Ideal	Electrical Resistivity micro ohm cm		Core Density after swage
		Composite	Core	% Ideal
11,400	43	2.00	10	77
15,900	48	2.12	0	96

Several points in Table IX are worthy of comment. First, it is to be expected that a higher core density in the ampoule should result from a higher extrusion pressure and that the after-swage resistivity is lower. The zero resistivity shown in the table obviously is not valid but rather the result of a large percentage error which will be treated in detail later in this report. However, the surprising item is the fact that higher

starting core density produces a lower after swage density. No rationalization for this is apparent.

Table XI Electrical Resistivity of Swaged Wires filled with $CuCl_2$ Intercalated Superior 1601

Extrusion Pressure Pounds/in^2	Core Density grams/cm^3	Electrical Resistivity micro ohm cm	
		Composite	Core
9,100	2.42	2.11	7.3
11,400	2.27	2.13	∞

The "infinity" in the core column of the above table indicates that the core is contributing nothing to total conductivity. Again, the errors are probably controlling the experiment.

The following experiment was performed in an attempt to understand the relationship between the extrusion pressure and the resulting resistivity after swaging. Extrusions into copper ampoules were made with Lonza KS 44 and with Superior 2135 graphite powder. The core densities determined from weight and geometry and the ampoules swaged until longitudinal cracks appeared at which the wire resistivity was measured. Results follow:

Table XII Resistivity of Extrusion Filled Graphite Core Wires

Graphite	Extrusion Pressure Pounds/in^2	Initial Core Density % of Ideal	Area Reduction %	Resistivity micro ohm cm
KS 44-1	9,100	43	86	2.01
KS 44-2	13,600	51	88	2.05
KS 44-3	15,900	59	88	2.07
2135-1	9,100	37	88	2.03
2135-2	15,900	58	88	2.10
2135-3	29,500	71	88	2.18

With the even progression of values in the right hand column it is tempting to ascribe an increase in resistivity of the wire to an increase in extrusion filling pressure although the variation is within the range of error.

4. Copper Chloride Intercalated Graphite

A series of five copper tubes were filled by extrusion with copper chloride-intercalated KS 44 graphite. Measurements of the core resistivities were made using high (12 amp) currents. This was done to increase the accuracy of the core resistivity calculations.

Table XIII Resistivity of Extrusion Filled $CuCl_2$ Intercalated Graphite-Ampoules

Sample	Core Density gram/cc	Composite Resistivity micro ohm cm			Core Resistivity micro ohm cm		
		Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
Cu Tube #1	0	--	2.23	2.13	∞	∞	∞
Cu Tube #2	0	2.32	2.21	2.10	∞	∞	∞
#1	2.20	2.31	2.24	2.13	∞	∞	∞
#2	2.52	2.34	2.23	2.13	∞	∞	∞
#3	2.46	2.31	2.24	2.16	∞	∞	∞
#4	2.39	2.30	2.24	2.14	313	∞	∞
#5	2.39	2.29	2.22	2.11	51.3	∞	∞

Two unfilled copper tubes were used as controls. The calculated conductivity of the copper in these controls was used to determine the core resistivities of samples 1 to 5. As can be seen by the data, extrusion of a graphite core into a hollow copper tube is more likely to increase the total resistivity of the tube than to decrease it. These tubes were then swaged and resistivities are tabulated later in this report.

5. Conclusions

The data in this section are puzzling in their seeming to go against logic in some instances. However, it can be stated with certainty that

no technical advantages have been disclosed for the extrusion filling of ampoules for the swaging of intercalated graphite filled composite wires.

The swaging of copper sheathed intercalated graphite is a difficult art at best and no assurances can be given that reduction of area greater than 50% can be obtained. Much, much greater reductions are needed for a successful wire fabrication procedure. No indications were observed of beneficial pressure effects on intercalated graphite.

III. Fabrication of Composite Wires (continued)

B. Swaging

1. Introduction

Swaging, a metal working process which is described in reference 6 is a method of reducing the diameter of rods or wires by means of open faced reciprocating dies. When the rods being reduced are uniformly solid the reduction of diameter proceeds in a straight forward manner. However, when the rods are heterogeneous i.e. having a core of different material than the sheath, or in the extreme, a tube, then difficulties arise in the form of longitudinal cracks. While, on several occasions (6,14), heterogeneous rods have been successfully swaged through > 90% reduction of area there is no organized information in the literature to aid one in achieving that result consistently. However, there is reason to persist in the use of swaging to produce high conductivity composite wire with an intercalated graphite core since only that method has been observed to produce the high conductivity. It is possible that the high pressures encountered in swaging as opposed to wire drawing, for instance, are a significant factor. High pressure has been observed to produce beneficial results in other cases of intercalated graphite (15).

2. Swaging Experiments

Preliminary Experiment: To get an indication of the behavior of composite wires a number of different materials were loaded into copper ampoules and swaged. The starting diameters were 0.250" and uniformly it was found that longitudinal cracks developed by 0.087" diameter, so composite resistivities were measured at that point. Core resistivities were

calculated as described in reference 6. Results are tabulated below.

Table XIV Resistivities of Swaged Wires With Various Cores

Powder	Intercalant (stage)	Core Resistivity micro ohm cm		
1601 (graphite flakes)	None	15.3		
2135 (fine graphite powder)	None	7.96	800°C, 1 hr	51.4
2135 (150°C, 1 week)	None	29.8		
Cu powder	--	2.06	800°C, 1 hr	1.79
1601	$CuCl_2$ (II)	29.8		
2136	SbF_5 (II)	29.8		

The core resistivities appear to be quite variable and while the copper core responds well to annealing the graphite does not.

Thin walled tubes: The results of three swaging experiments using the large I.D (0.180") tubes and the modified extrusion die (III A 2- Modification 2) are as follows:

Table XV Swaging With Thin Walled Tubes. Starting Diameter = 0.250 Inches

Graphite	Intercalant	% Ideal Density at Start	Diam Where Cracks Appear	% Area Reduction	Extruder Used?
1601 (flake)	--	93.3	0.172"	44.1	Yes
2135 (powder)	--	72.3	0.125"	68.2	Yes
2135 (powder)	$CuCl_2$	35.7	0.094"	80.6	No

These experiments shown that the thin-walled tubes should not be used in the swaging experiments, as they crack too early.

Copper Ductility: It was thought that perhaps the annealed copper in the ampoules was being altered during swaging so as to decrease its ductility. If so, the resistivity of a swaged tube would also be expected to increase. To test this hypothesis a hollow copper tube was swaged until it closed at .094". Its resistivity was found to be 1.72 micro ohm cm, a value

well within experimental error of its actual value of 1.70 micro ohm cm. Although not direct proof, this is good evidence that the copper sheath maintains its ductility throughout the swaging process.

Small I.D. Tubes: After a long discussion with Mr. William Romanow, Manager of the Materials Processing Lab in the Laboratory for Research into the Structure of Matter at Penn, several useful facts came to light. In swaging copper tubes the wall thickens by 90% and elongates 10%. Thus when the center is packed with high density graphite the latter acts as a mandrel and the copper wall extends over it. Under these conditions 90% reduction in area should be possible. In a letter from Phelps Dodge we learned that annealed copper tubes of .404" O.D. x 0.1" thickness filed with graphite powder could be swaged to .125" without breakage, yielding a total area reduction of 90.4%. Calculations reveal that 74.5% of the initial cross-sectional area is copper. The "large I.D." copper tubes we had been using until recently were only 48.2% copper by area initially. Quite conveniently, we had on hand some OFHC tubing with a 76.2% cross sectional area percent of copper. This was used in the following experiments.

Table XVI Swaging of Thick Walled Tubes

Graphite	Intercalant	% Ideal Density of Graphite at Start	Diameter Where Cracks Appear	% Area Reduction	Extruder Used?
2135	--	39.5	0.081"	85.9%	No
2135	--	74.8	0.094"	80.8%	No

Fine Composite Wires: A copper ampoule was loaded by extrusion with Stage II SbF_5- intercalated #1601 graphite. After each pass through the

swager the resistance, outside diameter and length of the sample were measured, from which the composite resistivity could be calculated. The following results were found:

Table XVII Progress of Swaging of SbF_5 Intercalated Wire

Die Size inches	Resistivity - micro ohm cm Composite	Core	Core Density g/cc	Graphite Volume %
.250	2.12	13.6	2.14	21.2
.220	2.12(est)	*	*	*
.204	2.11	*	*	*
.187	2.12	*	*	*
.158	2.10	*	*	*
.141	2.13	*	*	*
.125	2.12	*	*	*
.110	2.13	*	*	*
.102(cracks)	2.12	∞	2.02	15.2

* Not Applicable

Resistance measurements could not be made on the wire until it was passed through the .204" die. However, since ρ seemed to be constant throughout the rest of the experiment, it was assumed that the original unswaged tube had a ρ=2.12 micro ohm cm. Swaging had the effect of decreasing this sample's core density and core volume fractions from their initial values. The core ρ increased because the volume fraction of copper increased while the total ρ stayed constant.

The #2135 graphite which had been intercalated with nitric acid was dried in a nitrogen atmosphere.. The procedure consisted of adding nitrogen gas at a pressure of one atmosphere to the container holding the intercalated powder. The pressure in the container was then decreased to about one-half an atmosphere by using a vacuum pump. This was repeated several times, and then the pressure was lowered to one-quarter of an atmosphere. After

several more of these cycles the container was evacuated to a pressure of less than one micron for several hours. The powder was then pressed into pellets for resistivity measurements via the contactless RF method. Using a pressure of 66,000 psi the resistivity was found to be 792 micro ohm cm and the density 1.88 g/cc.

The resistivity value obtained using nitric acid approximates that of copper (II) chloride as an intercalant.

The nitric acid intercalated graphite was also extruded into a copper tube and swaged. The results of this experiment were:

ρ(total)	ρ(core)	d(core)
2.11μΩ-cm	∞	0.59 g/cc

Three copper tubes were loaded from the extruder with Superior #2135 graphite intercalated with stage II SbF_5 at three pressures: low, intermediate, and high. These were the results:

Pressure	ρ(total)	ρ(core)	d(core)
9,100 psi	2.07micro ohm cm	196 micro ohm cm	3.16 g/cc
15,900 psi	2.26	∞	1.40
29,900 psi	2.26	8.33	4.59

Unidirectional Swaging: Three tubes were filled via the extruder with Superior #2135 graphite powder at different pressures. Each wire was swaged, by feeding the tube into the dies from one direction only and composite resistivities were measured.

Wire #	Initial Core Density (% of Ideal)	ρ Total (micro ohm cm)
1	37.1	2.03
2	57.5	2.10
3	71.2	2.18

The most loosely packed tube showed the lowest composite resistivity. All three wires cracked at the same die size, .079 inch, although wire #3 had more cracks than #2 which had more cracks than wire #1. The percent area reduction before cracking of these wires was 87.9%.

Swaging of $CuCl_2$ Intercalated Graphite

Five copper ampoules filled with $CuCl_2$ intercalated Lonza KS 44 were swaged, and their resistivities were measured after each swaging step. Two of these swaged wires were analyzed for copper content so as to determine core resistivity and density. Pressed samples of unintercalated and intercalated Lonza KS 44 and Superior #2135 graphites were measured for c-axis resistivities. This was done to help understand the condition of the core inside each swaged wire.

The results obtained from the five copper tubes are shown below:

Table XVIII Changes in $CuCl_2$-Graphite Core Wire on Swaging

Die	Composite Resistivity-micro ohm cm				
Die	Tube #1	#2	#3	#4	#5
before swaging	2.13	2.13	2.16	2.14	2.11
.228 inch	2.07	2.05	2.08	2.07	2.07
.204	2.12	2.13	2.14	2.11	2.09
.187	2.08	2.10	2.13	2.06	2.08
.158	--	2.12	2.17	2.12	2.12
1.41	2.14	2.14	2.18	2.13	2.14
.125	2.13	2.14	2.16	2.13	2.14
.110	2.15	2.15	2.18	2.12	2.13
.102	2.14	2.14	2.17	2.19	2.12
.094	2.15	2.16	2.16	2.13	2.13
	Core Density (g/cc)				
before swaging	2.20	2.52	2.46	2.39	2.39
after swaging				1.93	2.15
	Volume Fraction of Intercalated Graphite (%)				
before swaging	21.7	21.7	21.5	21.5	21.8
after swaging				33.7	29.8

	Core Resistivity (μΩ-cm)				
before swaging	∞	∞	∞	∞	∞
after swaging				4.08	4.95

These data indicate that swaging tends to decrease initial core density and increase its volume fraction. Core resistivity decreases to a very low value.

3. Graphite Fiber Cores

A single exploratory experiment was performed wherein Thornel "P" fibers having an average resistivity of 250 micro ohm cm were loaded into the cavity of a copper ampoule and swaged from 0.250" down to 0.087" diameter. This resulted in a sound, well integrated wire having a composite resistivity of 2.14 micro ohm-cm. Assuming that some degree of continuity of the fibers is maintained it is possible that structural members of high conductivity could be made this way. Time did not permit detailed follow up of this experiment.

III. Fabrication of Composite Wires (cont.)

C. Measurements on Swaged Wire

1. Introduction

It is evident from the spotty nature of the data presented so far that conclusions are difficult to draw. This section is intended as a review and summary of all the data to allow an explanation of the irregularity of the trends encountered.

2. Analysis of Core Errors

Two copper tubes filled with Superior #2135 graphite were swaged. Both were cut into five sections. The area taken up by the graphite core of each section was then measured under a microscope equipped with a micrometer. The lengths and masses of each section were recorded. An example of some of the measurements and subsequent calculations are given below:

length of sample L = .899 inch

average area of graphite core A = .005486 cm^2

mass of sample M = .7982 gm

diameter of wire D = .0949 inch

volume of graphite core $V_g = AL$

$= .0125\ cm^3$

total volume of sample $V_T = \pi \left(\frac{D}{2}\right)^2 L$

$= .1042\ cm^3$

copper volume $V_C = V_T - V_g$

$= .0917\ cm^3$

copper mass $M_c = (8.96\ g/cc)\ V_c$

$= .8214$ gm

It can be seen that M_C exceeds the total measured mass of the wire by .0286 gm. This error occurs regularly in the data. This method was also found to be very tedious and too dependent on judgment to be considered accurate.

3. Analysis of Externally Swaged Wire

A set of measurements was performed on two composite wires of 0.04" diameter which were sent to us by Mohamed Mohamdein at Phelps-Dodge. One contained Superior #2135 graphite intercalated to stage II with SbF_5. The other contained unintercalated #2135 graphite. Both wires were swaged and drawn from 0.405" outside diameter copper tubes. The tubes were swaged to 0.200" diameter, followed by annealing at 850°F for ½ hour. The tubes were then drawn down to 0.04" diameter and annealed at 950°F for ½ hour. The following results were obtained:

Sample		ρ(total)	ρ(core)	d(core)
unintercalated		1.80 micro ohm cm	∞ micro ohm cm	0 g/cc
intercalated	front	2.64	38.4	4.10
	middle	2.73	∞	3.15
	end	2.61	42.4	4.10

The wires we received were quite long (approximately ten feet), so resistance measurements were made on sections about two feet in length from the middle and ends of each wire. Analytical measurements for copper were made on pieces about four inches in length from these same sections.

The calculations show that the first wire, made from a tube filled with unintercalated graphite, apparently had little graphite in its core, on the order of 1.5% by volume. This graphite does not appear to contribute to the conductivity of the sample. The second wire did have a core, about 33.4% volume percent intercalated graphite on average. Of the three sections of this second sample which were measured, two had reasonable core resistivities and high core densities.

The core of the middle section apparently did not contribute to the conductivity of that section. A reason for concern is the disparity between the calculated core densities of the second sample and the theoretical density of stage II SbF_5-graphite, which is 2.577 g/cc.

4. Recapitulation of Data

Data on all previously swaged wires were compiled and measurements made to determine their core densities and core resistivities. Samples of approximately four inches in length were cut from the center of each swaged wire. The length and mass of these samples were recorded, and the outside diameter of each sample was measured in five places and averaged. The mass of the copper sheath of each sample was then determined by atomic absorption. These measurements were made with a Jarrel-Ash model 810 atomic absorption spectrophotometer. A computer program was written to reduce the data, and the results are summarized in Table XIX.

Table XIX Summary of Measurements on Swaged Wires

Date	Graphite	Intercalant	Resistivity - micro ohm cm		Core Density g/cm^3	Extruded ?
			Composite	Core		
11/20/79	1601	None	2.71	∞	1.98	N
11/27/79	2135	None	2.52	∞	0.56	N
12/5/79	2135	None	2.48	∞	0.71	N
12/5/79	1601	$CuCl_2$	2.62	∞	0.15	N
12/13/79	2135	SbF_5	2.32	∞	0.12	N
1/3/80	1601	None	3.53	∞	0.75	Y
1/3/80	2135	None	3.18	13.5	3.13	Y
1/11/80	2135	$CuCl_2$	2.35	2.79	6.58	N
3/19/80	2135	None	1.92	7.10	4.47	N
3/20/80	2135	None	2.17	∞	0.14	N
4/1/80	2134	None	2.64	∞	3.59	N
4/2/80	2135	None	2.16	10.5	3.73	Y
4/25/80#1	2135	None	2.00	9.31	3.89	Y
4/25/80#2	2135	None	2.08	∞	2.07	Y
5/9/80	1601	$CuCl_2$	2.11	7.30	4.22	Y
5/12/80	1601	$CuCl_2$	2.13	∞	2.27	Y
5/23/80	2135	HNO_3	2.25	98.4	3.97	Y
6/30/80	2135	None	1.80	∞	0	N
6/30/80	2135	SbF_5	2.63	40.4	3.10	N
7/8/80	1601	SbF_5	2.12	∞	2.02	Y
7/16/80	2125	HNO_3	2.11	∞	0.59	Y
7/16/80	2135	SbF_5	2.07	196	3.16	Y
7/18/80#1	2135	SbF_5	2.26	∞	1.40	Y
7/18/80#2	2135	SbF_5	2.26	8.33	4.59	Y

Several general observations can be made from the data. First, many of the core densities seem too high. Second, the extruder appears to aid in producing cores that are not insulators (a resistivity of ∞ indicates that the core does not contribute to the conductivity of the sample and hence acts as an insulator). Seven of the thirteen extruded samples had finite core resistivities, while three out of eleven unextruded samples had finite core resistivities. Also, there seemed to be little dependence of core resistivity on whether the core material was or was not intercalated. Six of the twelve intercalated graphite cores gave finite core resistivities, while four of the twelve unintercalated graphite cores gave finite resistivities. Another observation is that cores of #1601 graphite flakes tended to be insulators (5 out of 6 times), while cores of #2135 graphite powder, intercalated or unintercalated, gave finite resistivities (9 out of 18 times). These results indicate that further experiments can be made with extruded, unintercalated #2135 powder.

An analysis of the measurements on a copper tube filled with #2135 graphite and swaged on 4/2/80 was performed. The measurements on this wire with estimated errors are:

L=5.3± .1cm (length of wire used for resistance measurements)

O.D.=0.23922± .005 cm (outside diameter of wire)

R=0.2551± 0.0075 mΩ (resistance of piece of wire with length L)

M=3.56994± 0.01 gm (mass of wire of length LL)

C=88.15± 1.0% (percent of copper by mass in wire)

LL=4.063± 0.1 inch (length of wire used for analytical test for copper)

B=99.25± 1.0% (percent of copper in all-copper "control" wire)

The worst case calculations for V_{Cu} (volume fraction of copper in the wire), V_G (volume fraction of graphite in the wire), ρ (core resistivity) and d (core density) follow:

	V_{Cu}(%)	V_G(%)	ρ(μΩ-cm) core	d(gm/cc) core
normal calculation	75.7	23.1	10.5	3.73
worst case (+)	80.3	29.7	∞	5.60
worst case (-)	69.9	15.7	3.42	2.50

Each worst case value was calculated separately. The core resistivity appears to be a particularly difficult value to determine accurately. The core density values are still high, even in the lowest worst case value.

5. Conclusions

As a general matter it is ineffective to determine the resistivity of a core in a composite wire sheathed in copper. When the resistivity of the core is larger than that of copper and its volume percent is 25% or less, the overall error in the measurement (5%) is equal to or greater than the conductivity contribution of the core. Thus a significant measurement can be made only when the core resistivity is equal to or less than that of the sheath. That condition did not appear to be satisfied in this study.

D. Rolling Experiment

A rolling experiment was attempted to determine if this method has advantages over swaging. A copper ampoule was filled with Superior #2135 graphite and passed through a motorized rolling device thirteen times, each time moving the rollers closer by .02 inches. The ampoule lengthened by a factor of three, widened by a factor of two and became seven times thinner. Composite resistivity was calculated to be 2.6 4 micro ohm cm, which is a comparatively high value. On the basis of this number it was decided not to continue the rolling experiments.

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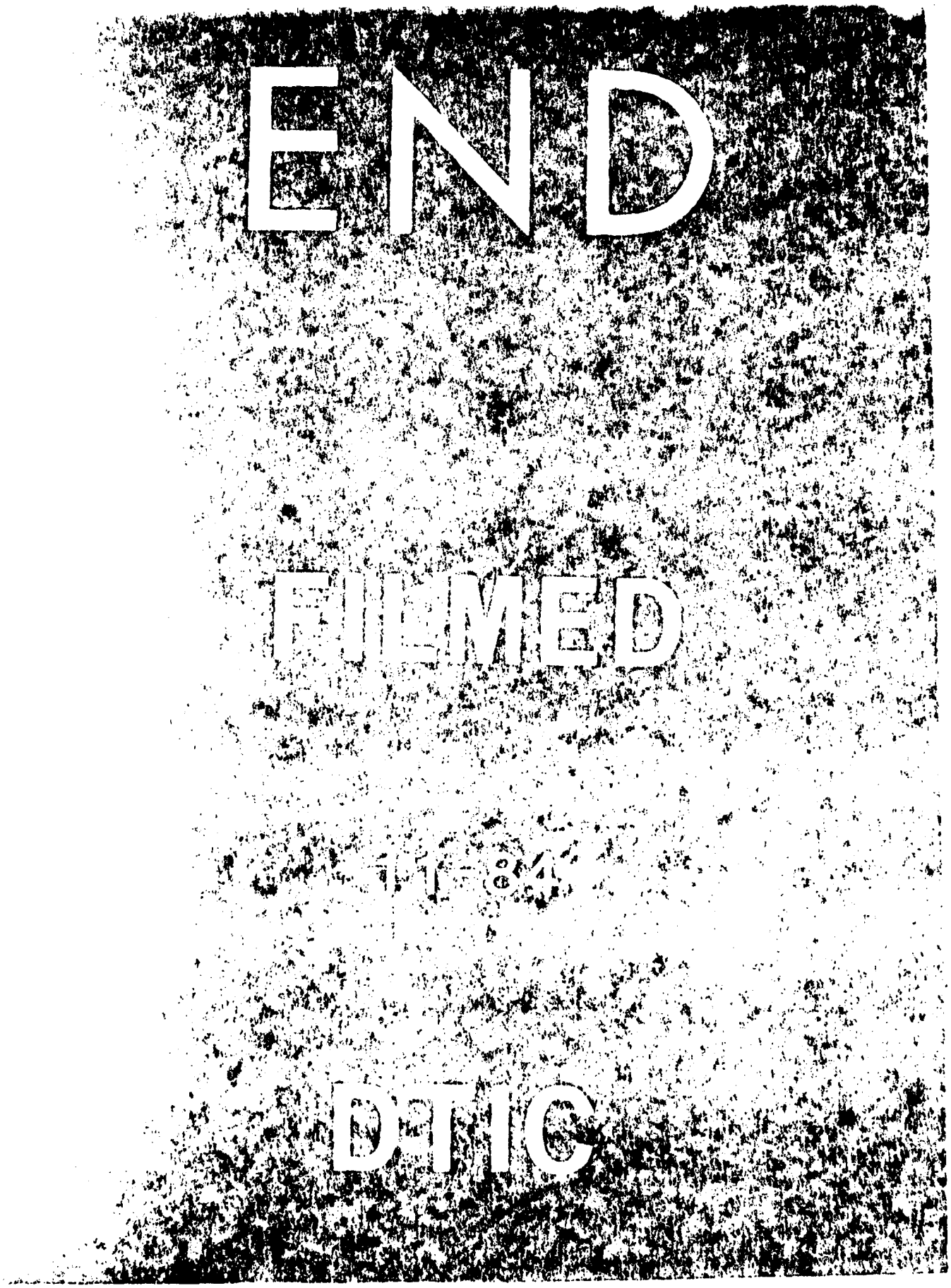
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